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THE ESTIMATION OF CHLORIDE BY MEASURING THE E. M. F. OF A SILVER, SILVER CHLORIDE, CHLORIDE ION HALF CELL FOR THE PURPOSE OF ESTIMATING H OR OTHER TOXICS

to
February 6, 1945
by

J. Brockman and T. Lee
for
E. H. Swift and Carl Niemann

Report OSRD No. 4798
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THE ESTIMATION OF CHLORIDE BY MEASURING THE E. M. F. OF A SILVER, SILVER CHLORIDE, CHLORIDE ION HALF CELL FOR THE PURPOSE OF ESTIMATING H OR OTHER TOXICS

Service Directive: CWS-6

Endorsement (1) Morris B. Jacobs, Technical Aide, Division 9 to Dr. Walter R. Kirner, Chief, Division 9.

Forwarding report and noting:

"A method for (1) determining the chloride concentration in an aqueous solution by measuring the potentional of a cell composed of a reference half cell and a silver, silver chloride, chloride ion half cell, and (2) determining H or HN3 by liberating chloride by hydrolysis or by oxidation and then estimating the chloride is described. This method, for a solution of the appropriate acidity and ionic strength, takes about 2-3 minutes. The estimation is made with 10 ml. of solution and is accurate to about 4% for chloride concentrations of about 8 micrograms of H per ml. and to about 4-8% for concentrations between 0.79 micrograms of H and 8 micrograms of H per ml. The procedure and apparatus are described. The factors which influence or interfere with the determination are discussed. The procedures used to liberate chloride from H which has been collected on silica gel or charcoal, or in diethyl phthalate or acidified potassium permanganate solution (the latter an absorbent not previously described) are detailed. The effectiveness of these absorbents and solutions in removing H vapor from air is considered. Procedures are also given for the determination of HN3 using diethyl phthalate or 0.25 F nitric acid as bubbler liquid."

(2) from Dr. Walter R. Kirner, Chief, Division 9 to Dr. Irvin Stewart, Executive Secretary of the National Defense Research Committee.

Forwarding report and concurring.

This is a progress report under Contract 9-256, OEMsr-325 with the California Institute of Technology.

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Abstract

This report describes a method for 1) determining the chloride concentration in an aqueous solution by measuring the potential of a cell composed of a reference half cell and a silver, silver chloride, chloride ion half cell, and 2) determining H or HN3 by liberating chloride from it by hydrolysis or by oxidation and then determining the chloride. The determination of chloride in a solution of the appropriate acidity and ionic strength takes about 2-3 minutes. The determination is made with 10 ml of solution and is accurate to about 4% for chloride concentrations above 10^{-4} formal (corresponding to 8 micrograms of H per ml) and to about 4-8% for concentrations between 3×10^{-5} and 10^{-4} formal. The determination of chloride could be adapted to the analysis of other toxics containing chlorine.

In Part I the procedure and apparatus used for the determination of chloride ion concentration are described, and factors which influence or interfere with the determination are discussed.

In Part II are described procedures used to liberate chloride from H which has been collected on silica gel or charcoal or in diethyl phthalate or acidified potassium permanganate solution. The effectiveness of each of these adsorbents and solutions in removing H vapor from air is considered.

In Part III, are given the results of experiments on the recovery of HN3 vapor from air using diethyl phthalate or 0.25 formal nitric acid as bubbler liquids. Procedures are given for the determination of HN3 in these liquids.

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Part I

ESTIMATION OF CHLORIDE

1. Procedure for Determining Chloride

Discussion

The concentration of a chloride solution was determined by measuring the potential of the cell:

$$Ag_{(s)}, AgCl_{(s)}, Cl^- \| Cl^-, Hg_2Cl_{2(s)}, Hg_{(l)}$$

The silver, silver chloride, chloride ion half cell consisted of a silver wire immersed in the chloride solution which was being analyzed; solid silver chloride, finely divided, was present as a suspension in this half cell. The mercury, mercurous chloride, chloride ion half cell was a reference half cell and consisted of a Beckman calomel electrode. The two half cells were connected together by a salt bridge of saturated ammonium nitrate solution. The potential of the cell was measured with a Beckman pH meter, and the concentration of chloride was obtained by comparing the potential with a calibration curve (see Figure 2).

This method is similar to a method used by Furman and Low (see reference (1)) for determining small concentrations of chloride in the presence of other salts.

Experimental

a. Procedure for Determining Chloride

APPARATUS: The titration cell is shown in Figure 1. The sample solution was contained in a 20 ml glass vessed with a convenient drain and plug at the bottom.

The reference half cell was a No. 270 Beckman calomel electrode. This dipped into the solution of the salt bridge, a saturated solution of ammonium nitrate contained in a glass tube. (This tube was made by sealing a 5 cm length of 2-3 mm tubing to a 4 cm length of 12 mm tubing. At the end of the smaller tube a sintered glass plug was formed by putting powdered glass in it and heating it. The sintered glass was fine enough so that the ammonium nitrate solution did not leak out rapidly.

The silver electrode was a 2-3 inch length of 12 gauge silver wire held at the upper end by an alligator clip; the lower end dipped into the solution to a depth of about 2 cm.

Also in the cell were a glass stirrer (driven by an electric motor) and a thermometer.

The calomel cell was connected to the lower jack of a Beckman Model G pH Meter. The alligator clip which held the silver electrode was connected by a shielded cable to the top jack.

PROCEDURE: A cell, described in Note 1, was assembled. The silver wire was cleaned by dipping it into 10 formal HNO_3 for 15-30 seconds and thoroughly rinsing it with distilled water (Note 1). 1.0 ml of 2.5 formal

HNO_3 was added to a solution to be analyzed (Note 2) and the solution was diluted to 10 ml. Meanwhile the cell had been allowed to drain. The solution was added to the cell. Two drops of $AgCl-NH_4OH$ reagent (Note 3) were added, and after 1-3 minutes the potential of the cell was measured with the Beckman pH meter. The amount of chloride was determined by comparing the potential with a calibration curve (Note 4).

Notes:

1. It was found that the potential of cell was affected by failure to clean the silver electrode. Attempts were made to clean the electrode by dipping it into ammonium hydroxide and by heating it in a flame to red heat; however, the treatment with nitric acid led to reproducible cell potentials.

If the electrode was not thoroughly rinsed with distilled water, silver nitrate was introduced into the sample solution and caused an error in the determination.

2. 0-9 ml of the sample may be taken. The calibration curve is a plot of the E.M.F. of the cell against the final concentration of chloride in the solution <u>after</u> it has been diluted to 10 ml.

3. A solution of silver chloride in aqueous ammonium hydroxide was used for the purpose of obtaining a finely divided suspension of silver chloride in the solution being analyzed; the solution being analyzed had been acidified and silver chloride precipitated when the $AgCl-NH_4OH$ reagent was added to it. The reagent was made by dissolving 0.072 g. of silver chloride in 1.7 ml of 6 formal ammonium hydroxide, diluting with water to 50 ml. It was 0.01 formal in silver chloride and 0.2 formal in ammonium hydroxide.

4. The potential of the cell was plotted against the log of the chloride concentration; the curve is shown in Figure 2. The nature of the curve is discussed in Section 2 below. In order to obtain data for the curve, the potential of the cell was measured when the cell contained potassium chloride solutions of the following concentrations: 5×10^{-3}, 5×10^{-4}, 2×10^{-4}, 1×10^{-4}, 8×10^{-5}, 6.5×10^{-5}, 5×10^{-5}, 4×10^{-5}, 3×10^{-5}, 2×10^{-5}, and 1×10^{-5} formal. Since the curve (see Figure 2) is not linear below 10^{-4} formal, many more points have to be taken in this region.

Once this calibration curve is made, other calibration curves can be constructed from day to day, merely by measuring the potential of one concentration of chloride and drawing the curve parallel to the established calibration curve. This is discussed in Section 2.

Figure 1. Diagram of the Cell

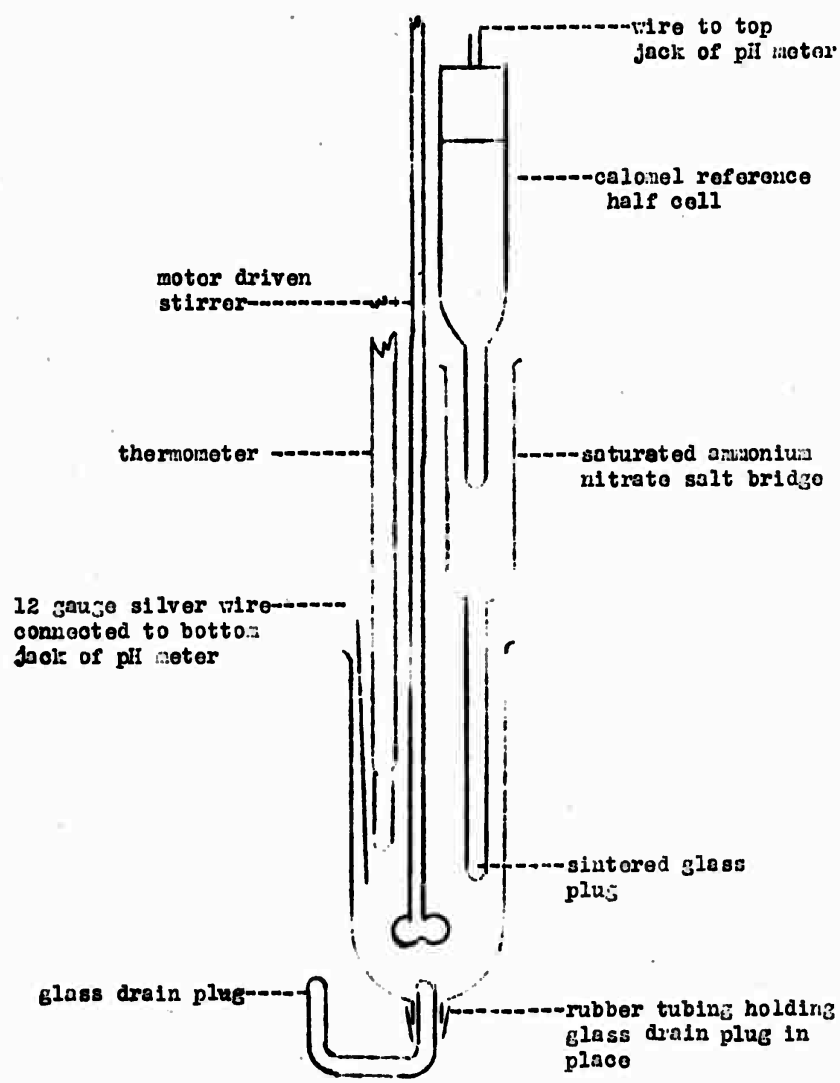

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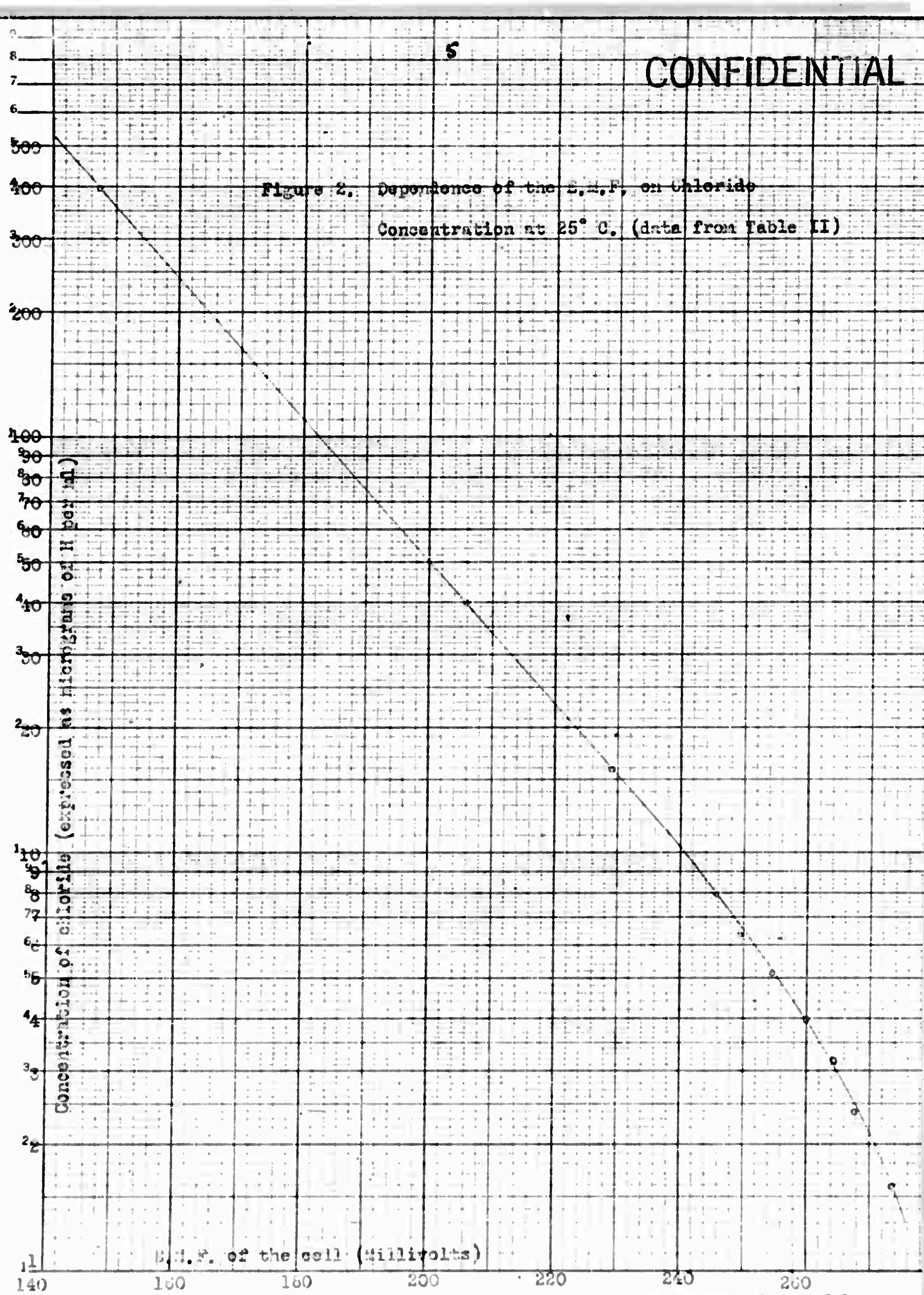
Figure 2. Dependence of the E.M.F. on Chloride Concentration at 25° C. (data from Table II)



2. Factors Affecting the Determination

Discussion

It would be expected that the potential of the cell would be influenced not only by the concentration of chloride in the solution of the silver chloride half cell, but also by 1) the ionic strength of that solution, 2) the hydrogen ion concentration, 3) interfereing constituents, such as ions or molecules that react with silver or chloride ions, 4) the temperatures of the two half cells, and 5) condition of the reference electrode, of the salt bridge, and of the silver wire electrode. These factors are considered below, especially for the purpose of ascertaining how carefully each must be controlled in order to avoid appreciable errors.

Measurement of the potential involves the precision of the meter. The sensitivity of the Beckman pH meter when used carefully is about 1 millivolt; that is, an error of 0-1 millivolt can be expected even in a careful determination; therefore, in the sections below, errors less than about 0.5 millivolt are considered to be insignificant.

a. The dependence of the E.M.F. on the concentration of chloride.

Since the electromotive force of the calomel half cell is constant, the electromotive force of the cell is determined by the half cell

$$Ag + Cl^- = AgCl + e^-. \qquad 1$$

At 25°C

$$E_{half\ cell} = E_0 + 0.059 \log [Cl^-] \qquad 2$$

Therefore, it would be expected that if the electromotive force of the cell is plotted against the logarithm of the chloride ion concentration, a straight line would result. The empirical curve obtained by using the procedure in Section 1 to obtain the potentials corresponding to chloride solutions of various concentrations is shown in Figure 2.

In the straight portion of the curve, a change in potential of 59 millivolts is obtained for a ten-fold change in chloride ion concentration, a change which would be predicted from equation 2 . Assuming that 2 is true, it can be shown that the change in chloride ion concentration required to change the potential of the cell by an amount ΔE is:

$$\%\ \text{change in}\ [Cl^-] = -1 + \text{antilog}\left(-\frac{\Delta E}{0.059}\right)$$

thus a change of 4% in chloride concentration corresponds to a change of 1 millivolt. This means that an error of 1 millivolt in the determination of the potential will correspond to an error of 4% in the determination of chloride concentration. Since most of the sources of errors in the determination cause changes in the potential which are independent of the particular chloride ion concentration being measured, most of the errors will be relative errors, and will always be a certain percent of the total amount of chloride present, rather than a certain number of micrograms of chloride; thus, the error caused by the limited sensitivity of the meter will be from 0-4% of the chloride present.

$[Cl^-]$ in equation (2) is the total chloride concentration, the sum of chloride from the sample and from the silver chloride. The abscissa axis of the calibration curve represents, however, the chloride from the sample only. For samples containing a large amount of chloride the additional chloride from the silver chloride is negligible and the curve is a straight line; but if the amount of chloride from the silver chloride is comparable to the amount of chloride from the sample[1], the curve is not straight and the sensitivity of the potential to chloride from the sample is smaller. This is seen in the empirical curves in Figures 2 and 3. The curves are straight above 10^{-4} formal (equivalent to 7.95 micrograms of H per ml).

The error caused by one millivolt when the chloride concentration is 3×10^{-5} formal is about 8%. It is impractical to use the method for determining concentrations below 10^{-5} formal (equivalent to 0.79 micrograms of H per ml).

b. The effect of ionic strength on the E. M. F.[2]

In the procedure described in Section 1 nitric acid is added to the sample solution so that the final concentration is 0.25 formal in nitric

---

[1]The chloride ion concentration of saturated silver chloride solution at 25°C is about 1.3×10^{-5} formal.

[2]The ionic strength is defined as 0.5 cz^2 where c is the concentration of each ion and z is the magnitude of the charge which the ion possesses.

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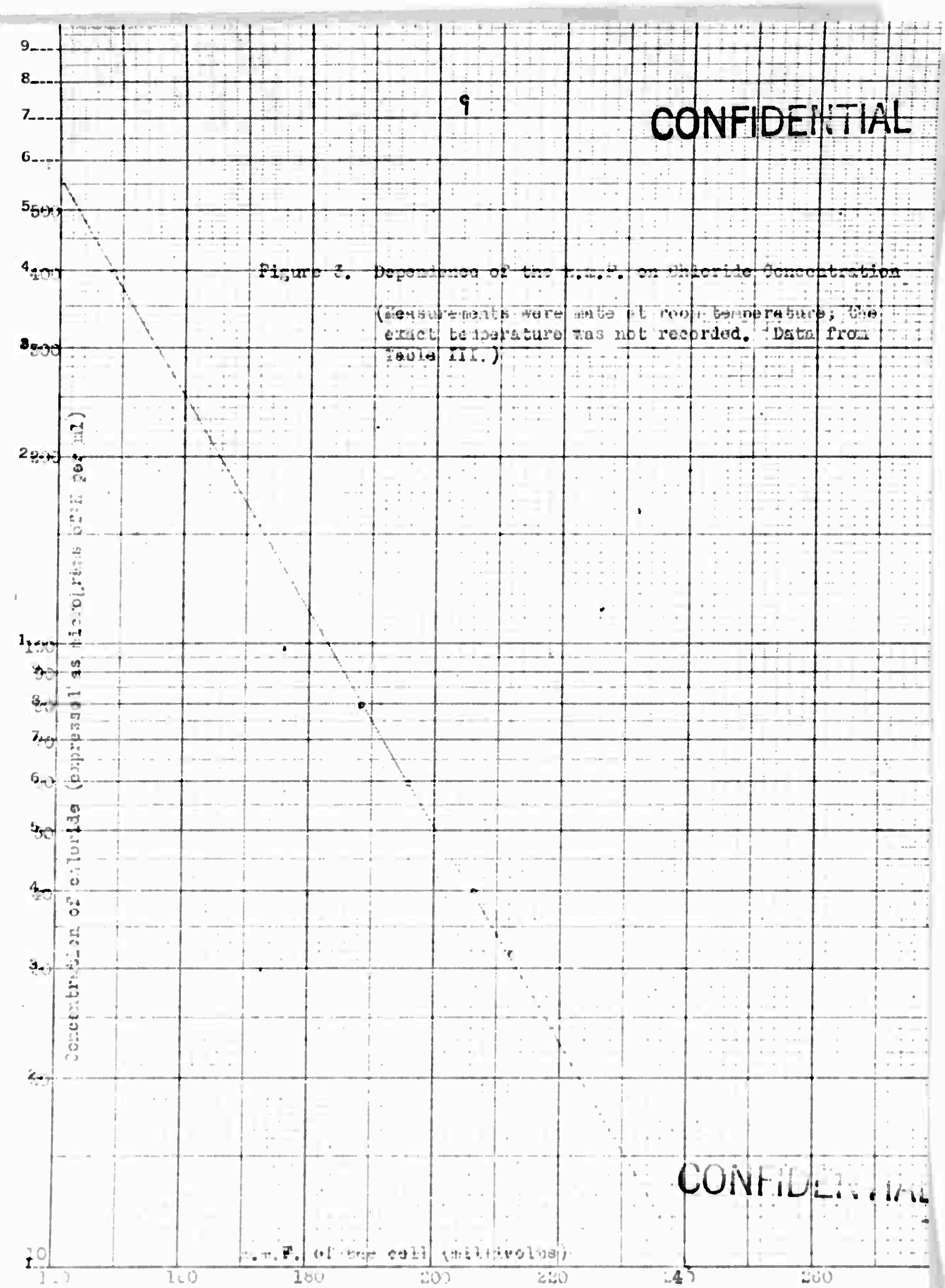

Figure 3. Dependence of the E.M.F. on Chloride Concentration

(Measurements were made at room temperature; the exact temperature was not recorded. Data from Table III.)

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acid. If the sample contains only hydrolyzed H, or only sodium or potassium chloride, then the ionic strength will be about 0.25, but if the sample contains appreciable amounts of other ionizable solutes, the ionic strength will be greater.

Therefore, in order to investigate how closely the ionic strength must be controlled, a series of measurements were made in which the ionic strength was varied from 0.25 to 1.00, the chloride ion concentration and the hydrogen ion concentration being held constant. It was found that the potential of the cell varies only 1-4 millivolts, an amount which would cause an apparent change in the chloride concentration of about 4-16%.

c. The effect of hydrogen ion concentration on the E. M. F.

A certain amount of acid must be added to the solution being analyzed in order to neutralize the ammonium hydroxide in the NH_4OH-$AgCl$ reagent. Moreover, a hydrogen ion concentration of from 0.1-0.5 molal seems desirable from the point of view of reproducibility in some of the procedures described in Part II. In a series of careful experiments with a cell of a similar type[1], Furman and Low (1) used 0.25 formal nitric acid. This concentration of nitric acid was chosen for the procedures in Section 1 and in Part II, without an investigation of the advantages of other acidities or another acid.

[1] The cell used by Furman and Low has a silver-silver chloride electrode and does not involve the use of NH_4OH-$AgCl$ reagent.

Experiments were made, however, to investigate the dependence of the potential of the cell on the hydrogen ion concentration; that is, measurements of the potential were made at different hydrogen ion concentrations, the ionic strength and the chloride concentrations being held at fixed values. These experiments show that for the determination of high (see Table II in the Experimental part) concentrations of chloride the hydrogen ion concentration can vary from 0.05 to 0.25 without causing a change in the potential of more than 1 millivolt (which corresponds to an apparent change of 4% in the chloride concentration). The hydrogen ion concentration is more critical in the determination of small amounts of chloride; and changing it from 0.05 to 0.25 molal caused an apparent change of 8% in the concentration of 5.10^{-5} molal chloride[1]. There is evidence that when the cell contains no chloride except that from the solubility of AgCl, the potential of the cell is quite dependent upon the hydrogen ion concentration.

d. The effect of interfering substances on the E. M. F.

The presence of ions or molecules which might interfere with the determination of chloride depends upon the source and treatment of the sample. For example, if H vapor is collected in potassium permanganate solution, and if the solution is treated by the procedure in Section 4, Part II, manganous ion will be present in the silver chloride half cell.

---

[1] 5×10^{-5} molal chloride is equivalent to 3.99 micrograms of H per ml.

The effects of manganous ion, acetic acid, and thiodiglycol are discussed in Part II and data from experiments investigating them are given.

e. The effect of temperature on the E. M. F.

The potential of the cell would be expected to be dependent upon the temperature in accordance with the Gibbs Helmholtz equation. The dependence was investigated empirically by putting the cell in a large box, the inside of which was maintained at a constant temperature, and measuring the potential for different concentrations of chloride. A series of measurements were made at each of four temperatures, 20°, 25°, 30°, and 40°C.

The data (see Figure 4) showed that the intercept of the calibration curve changed considerably with the temperature. The slope of the straight portion of the curve also changed. At 20° the slope was 57.6 millivolts per 10 fold change in chloride concentration; at 25°, 58.8 millivolts; at 30°, 60 millivolts, and at 40°, 60 millivolts.

In the analysis of samples of H in Part II the temperature effect was taken into account by using a calibration curve constructed at one temperature and then correcting potentials from sample analyses to that temperature. The corrections were made according to Table I.

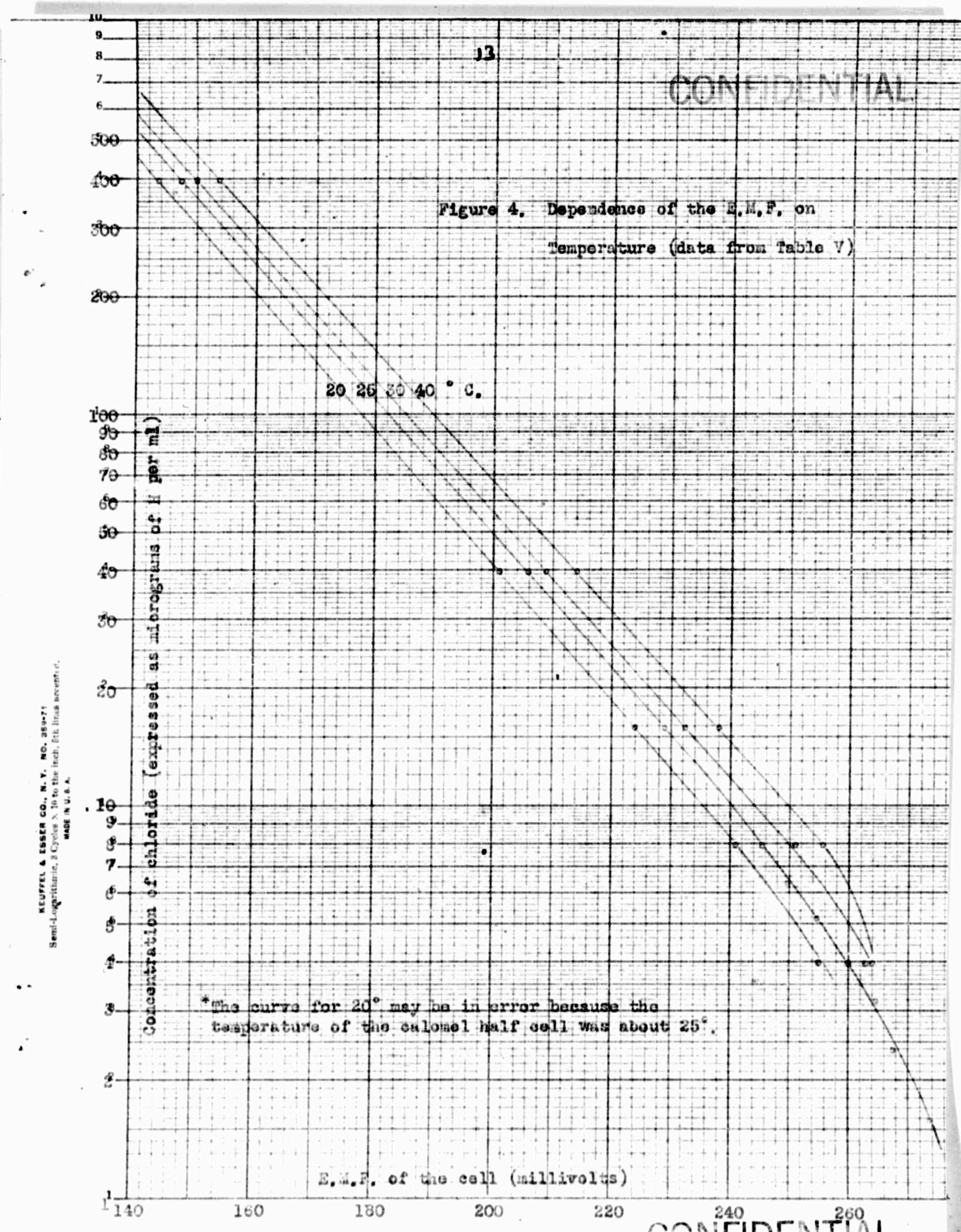
Figure 4. Dependence of the E.M.F. on
Temperature (data from Table V)
20 25 30 40 ° C.
Concentration of chloride (expressed as micrograms of H per ml)
*The curve for 20° may be in error because the
temperature of the calomel half cell was about 25°.
E.M.F. of the cell (millivolts)
140
160
180
200
220
240
260
1
2
3
4
5
6
7
8
9
10
20
30
40
50
60
70
80
90
100
200
300
400
500
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Table I

Corrections of Potentials for Temperature Increases of One Degree

Molality of chloride solutions	Corresponding γ of H per ml of solution[a]	Corrections to be subtracted from the observed potential (millivolts)		
		20-25°C	25-30°C	30-40°C
1×10^{-4}	7.95	1.2	0.8	0.4
2 "	15.9	1.0	.6	.5
5 "	39.8	1.0	.6	.5
5×10^{-3}	398	.6	.6	.3

[a] The concentration of H that gives on complete hydrolysis or decomposition the specified molal concentration of chloride.

Thus, if a calibration curve were constructed at 27° and if a potential measurement of a sample 10^{-4} formal in chloride were made at 25°, 2 x 0.8 or 1.6 millivolts would be added to the observed potential and the chloride concentration corresponding to the corrected potential would be read on the curve. An alternative procedure for correcting for temperature effects is described in f below.

f. Condition of the reference electrode, of the salt bridge, and of the silver wire electrode.

The potential given when a certain sample of chloride was analyzed varied from day to day by as much as 5 millivolts even though the temperature at which the measurements were made was the same. Perhaps this was due to slow changes in the liquid junction potential in the sintered glass plug of the NH_4NO_3 bridge. The effect of this variation was nullified by constructing a new calibration curve each day. The calibration curve was made merely by measuring the potential of a known concentration of chloride, plotting the corresponding point on semilog coordinate paper, and drawing a curve parallel to a calibration curve already established. That is, the slope of the curve was assumed to be independent of day to day changes in the reference electrode, etc., and the intercept was determined by analyzing a chloride solution of known concentration. One standardization for each day was sufficient.

This method of constructing a new calibration curve from the measurement of the potential for only one chloride concentration can also be used to eliminate errors due to temperature changes, provided the temperature changes are not large. A calibration curve is determined at one temperature; the potential given by a known concentration of chloride is measured at another temperature and a calibration curve for this temperature is drawn parallel to the curve already constructed.

Experimental

a. Concentration of chloride

Ten ml of an aqueous solution 2.5 formal in HNO_3 and the specified (see Table II) formality in KCl were analyzed by the procedure in Section 1. The results are shown in Tables II and III and Figures 2 and 3.

Table II

Dependence of the E. M. F. on Chloride Concentration

Molality of chloride	Corresponding concentration of H* (γ of H per ml)	Temperature of calomel half cell (°C.)	Temperature of AgCl half cell (°C.)	Observed E.M.F. (mv)
1×10^{-5}	0.79	25.0	25.0	280
2 " "	1.59	25.0	25.2	273.5
3 " "	2.39	25.1	25.3	267.5
4 " "	3.18	25.1	25.5	264.5
5 " "	3.98	25.0	25.5	260
6.5 "	5.16	25.0	25.5	254.5
8 " "	6.36	25.0	25.5	249.5
1×10^{-4}	7.95	25.0	25.5	245.5
2 " "	15.9	25.0	25.0	229
5 " "	39.8	25.0	25.0	206
5×10^{-3}	398	25.0	25.0	147.5

Table III

Dependence of the E. M. F. on Chloride Concentration
(The determinations were made at room temperature; the exact temperature was not recorded)

Molality of chloride	Corresponding concentration of H (as γ of H)	Observed E.M.F. (millivolts)
1.25×10^{-4}	9.9	241
2.0 " "	15.9	229
3.0 " "	23.9	219
4.0 " "	31.8	212.5
5.0 " "	39.8	206.5
7.5 " "	59.6	196
1.0×10^{-3}	79.5	188.5
5.0 " "	398	148.5

*The concentration of H that gives upon complete hydrolysis or decomposition the specified molal concentration of chloride.

b. Ionic strength.

One ml of KCl solution (10^{-2} or 10^{-3} formal) was added to water. The appropriate amounts of 2.5 formal HNO_3 and of 1 formal $NaNO_3$ were added and the solution was diluted to 10.0 ml. The potential of the cell was measured; the results are shown in Table IV.

Table IV

Effect of Ionic Strength on Potential

Molality of chloride	Ionic strength*	Molality of hydrogen ion	Room temperature (°C)	Observed Potential (mv)	Potential, corrected to 22.0°C.** (mv)
1×10^{-4}	0.15	0.15	22.5	237.5	237
	.25	.25	22.0	237	237
	.35	.25	22.0	238	238
	.50	.25	21.5	237.5	238
	1.00	1.00	22.0	239.5	239.5
1×10^{-3}	.15	.15	22.2	181	181
	.25	.25	22.2	181	181
	.35	.25	22.2	182.5	182.5
	.50	.25	22.0	184	184
	1.00	.25	21.8	184	184
	1.00	1.00	22.2	184	184

c. Hydrogen ion concentration

One ml of KCl solution was added to water. The appropriate amounts of 2.5 formal HNO_3 and of 1 formal $NaNO_3$ were added, and the solution was diluted to 10 ml. The potential of the cell was measured. The results are shown in Table V.

*See note 1 to page 8.
**See Table I, page 14.

Table V

Effect of Hydrogen Ion Concentration on Potential

Molality of chloride	Molality of hydrogen ion	Ionic strength*	Room temperature	Observed potential (mv)	Potential, corrected to 19.0°C** (mv)
5×10^{-5}	0.05	0.25	19.0	251.5	251.5
	.15	.25	19.5	253	252.5
	.25	.25	19.5	254	253.5
1×10^{-4}	.05	.25	19.5	238.5	238
	.15	.25	19.5	238	237.5
	.25	.25	19.0	239.5	239
2×10^{-4}	.05	.25	19.0	223	223
	.15	.25	19.5	222.5	222
	.25	.25	19.5	223	222.5
5×10^{-3}	.05	.25	19.5	144	143.5
	.15	.25	19.5	143.5	143
	.25	.25	19.0	143	143

d. Temperature

These determinations were made by the procedure as in a above. During these determinations the cell was kept in a large closed wooden box equipped with a heating coil, a large fan, and glass windows through which the thermometers could be read. The current for the heating coil was supplied by a variable transformer. The electrodes of the cell were connected to the pH meter by two shielded wires. The pH meter was not in the box, but was operated at room temperature. In order that the solutions being analyzed and the NH_4OH - AgCl reagent would be at this proper temperature they were kept in the box for 15 to 30 minutes before

*See note 1 to page 8.
**See Table I, page 14.

the analysis. The temperatures of both electrodes were probably equal to the stated (See Table VI) temperature within 1°C. The results of these determinations are shown in Table VI and in Figure 4.

Table VI

Dependence of the E. M. F. on Temperature*

Molality of chloride	Corresponding concentration of H (as γ of H per ml)	Temperature of calomel half cell (°C)	Temperature of AgCl half cell (°C)	Observed E.M.F. (mv)
5×10^{-5}	3.98	40.	39	264
1×10^{-4}	7.95	"	"	255.5
2 " "	15.9	"	"	238
5 " "	39.8	"	"	214
5×10^{-3}	398	"	"	153.5
5×10^{-5}	3.98	30.5	30	263
1×10^{-4}	7.95	"	"	251
2 " "	15.9	"	"	232.5
5 " "	39.8	"	"	209
5×10^{-3}	398	"	"	150
5×10^{-5}	3.98	ca. 25	20	255
1×10^{-4}	7.95	" "	"	241
2 " "	15.9	" "	"	224
5 " "	39.8	" "	"	201
5×10^{-3}	398	" "	"	143.5

*Data for 25°C. are given in Table II.

Part II

DETERMINATION OF H

1. Determination of H Collected on Silica Gel

Silica gel and activated charcoal were used to collect H vapor from air. In these experiments about a ml of the granular solid was held in a small glass tube between plugs of glass wool. The tube has the advantages that it is lighter and more rugged than a bubbler. Silica gel, at least the type used in these experiments is unsatisfactory as an absorbent for H because the recovery is low at high humidities (See a below). Activated charcoal is a good adsorbent, but the charcoal that was used contained impurities that interfered with the analysis.

It is possible to determine the H collected by silica gel by hydrolyzing the H in an aqueous solution, then determining the chloride concentration. (See the procedure in c below). However, if the silica gel contains chloride or some other constituent which will be extracted during the hydrolysis and cause a potential at the silver electrode, the determination will be in error. Davco silica gel[1], 69514-200 R 4.75, was found to contain practically no chloride but did contain a significant amount of tripositive iron that could be slowly extracted with water or acid.[2] It was found, however, that alkaline solutions do not extract a significant amount of iron from the Davco gel. Therefore, the H was

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[1] Made by Davison Chemical Corporation, Baltimore, Maryland.

[2] The removal of iron from silica gel has been described (reference (2)). Analyses of commercial silica gels show that the iron content is from 0.002 to .024%.

hydrolyzed in an alkaline solution and the solution was acidified only after it had been separated from the gel.

It was found that thiodiglycol changed the potential of the cell, presumably because thiodiglycol forms a complex ion with silver ion (5). However, when the ratio of the number of moles of chloride ion to the number of moles of thiodiglycol is two or less, the error caused by thiodiglycol is negligible. Therefore, the amount of thiodiglycol given by hydrolysis of H does not interfere. The results of experiments with thiodiglycol are given in b below and in Table VIII.

A series of experiments were made in order to test the determination of H collected on silica gel. Air saturated with H vapor was passed through glass tubes containing silica gel and the gel was analyzed by the procedure described in c below. The average deviation (the average error regardless of sign) of the determinations in which 1.2 mg of H were collected was about 6%; part of the error may have been due to the uncertainty in the concentration of H in the air stream.

Experimental

a. The Recovery of H by Silica Gel. Davco silica gel, 69514-200 R 4.75, was used in these experiments. The average diameter of the gel particles was about 1.3 mm. Before being used the gel was allowed to come to equilibrium with air of a known humidity. For the experiments at 90% humidity the gel was allowed to stand for several days in a desiccator containing a saturated solution of sodium carbonate at room temperature; the air in the desiccator had a relative humidity of about 90%.

For one experiment the gel was equilibriated with air of 50% humidity by passing a stream of air (containing no H) of 50% humidity through it for 7 minutes. For one experiment the gel was dried in an oven at 110-115°C. for 6 hours.

An adsorption tube was prepared by inserting a plug of glass wool into a glass tube, adding the Davoo silica gel, and inserting another plug of glass wool.

An apparatus described elsewhere (4) was used to provide an air stream of known humidity and temperature and containing H vapor at a concentration of 50 micrograms per liter (± 5%). This air stream was passed through the tube of silica gel and then through a bubbler containing diethyl phthalate. The H vapor that passed through the gel was recovered in the bubbler. The diethyl phthalate was analyzed for H by the DB3 colorimetric method (5). The results are shown in Table VII.

b. The Effect of Thiodiglycol on the E. M. F. of the Cell.

The procedure for determining chloride (see page 2) was used except that the appropriate volume of 14 milligram per milliliter thiodiglycol solution was added to the cell just before the NH_4OH-AgCl reagent was added. The thiodiglycol which was used was Eastman technical β,β'-dihydroxyethyl sulfide, T 1224. The results are shown in Table VIII.

Table VII[d]

The Recovery of H by Silica Gel
(H concentration in air 50 micrograms per liter. Temperature of air 40°C.)

Humidity of air with which gel was equilibrated[a]	Size of gel column[b] (mm)	Humidity of air (%)	Flow rate (liters per min)	Time (minutes)	Amount of H delivered (γ)	Amount of H in effluent air (γ)	Recovery (%)
0	6 x 50	37	1	30	1500	less than 10	more than 99.5
50	"	"	"	"	"	" " "	" " "
90	"	90	2	"	3000	1500	50
"	"	"	1	60	"	1500	50
"	"	"	"	30	1500	900	40
"	6 x 100	"	2	"	3000	1000	67
"	"	"	1	60	"	1440	52
"	12 x 100	c "	"	30	1500	100	93
		"	"	"	"	220	85

[a]The silica gel was brought into equilibrium with air at this humidity before collection of H was begun.

[b]The first figure gives the inside diameter of the glass tube, the second gives the length of the column of gel.

[c]In this experiment the air stream containing H was passed through the gel for 30 minutes then the bubbler was replaced by another bubbler containing diethyl phthalate and the air stream containing H was again passed through the gel for 30 minutes. In this way the amounts of H in the effluent air after the first 30 minutes and after the second 30 minutes could be determined.

[d]The experimental work was done by Carl T. Redeman of this laboratory.

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Table VIII

Effect of Thiodiglycol on the E. M. F. of the Cell

Concentration of chloride (moles per liter)	Concentration of thiodiglycol (moles per liter)	Temperature (°C)	Observed E.M.F. (mv)	Error in the determination of chloride[1] (%)
0.5 x 10^{-4}	11.9 x 10^{-4}	23.5	251.5	-24
1.0 "	" "	"	240	-10
2.0 "	" "	"	226	- 4
5.0 "	" "	"	203	0
50.0 "	" "	"	147	+ 4
0.5 "	3.96 "	23.0	253	-18
1.0 "	" "	"	242	- 2
2.0 "	" "	"	226	- 4
0.5 "	1.59 "	"	257	- 2
1.0 "	" "	"	242	- 2
0.5 "	0.	"	257.5	-
1.0 "	0	"	242.5	-
2.0 "	0	"	227	-
5.0 "	0	"	203	-
50.0 "	0	"	146	-

c. Procedure for the Determination of H Collected on Silica Gel. Adsorption tubes were prepared as in a. The glass tubes were 8 mm O.D. and the length of the gel columns was 6 cm.

The H vapor apparatus (see a) was used to provide an air stream containing a known concentration of H (613 micrograms of H per liter). This air stream was passed through the tube at a flow rate of 1 liter per minute for 2 minutes, except in the first and second experiments in which

[1]Calculated from the fact that 1 millivolt error is equivalent to 4% (see page 7).

the times were zero and 117 seconds respectively. The concentration of H in the air stream was known to within about 5%.

The silica gel was transferred to a 15 ml centrifuge tube and 5 to 10 ml of water and 3 drops of 6 formal NaOH were added. The mixture was immersed in a bath of boiling water for 10-15 minutes and was stirred frequently. The mixture was centrifuged and the centrifugate was poured into a 25 ml volumetric flask*. The gel was washed two or three times with 2 ml portions of distilled water. To the flask were added 2.5 ml of 2.5 formal HNO_3. The solution was diluted to the mark and about 10 ml of the resulting solution were analyzed in the cell by the procedure on page 2 . The results are shown in Table IX.

Table IX

Determination of H Collected on Silica Gel

Amount of H collected[a] (micrograms)	Amount of H found (micrograms)	Error (micrograms)	Error (%)
0	40	+ 40	--
1195	1120	- 75	-6.3
1226	1350	+124	+10.1
"	1293	+ 67	+ 5.5
"	1330	+104	+ 8.3
"	1272	+ 46	+ 3.8
"	1260	+ 34	+ 2.8

[a]Calculated from the concentration of H in the air stream and the time of sampling.

*In a routine procedure the solution could probably be decanted from the gel without centrifuging first.

In an experiment in which the nitric acid was added to the centrifuge tube before the gel was separated from the solution 1020 micrograms of H were found; 1226 were collected.

2. Determination of H Collected on Charcoal.

R.A. Titt states that charcoal is an effective adsorbent for H even at high humidities. He found that the recovery by 5 cc of charcoal through which "dilute H vapor" in air at 32°C. and 95-100% humidity was passed at a rate of 10 liters per minute for 2 hours was greater than 99%.

H collected on charcoal can be determined by heating the charcoal with an aqueous solution and determining the concentration of the chloride in the solution by the method already described. A method similar to this in which the chloride solution is analyzed by a potentiometric titration with silver nitrate solution has been described.*

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*The determination of H collected on charcoal has been made by R.A. Titt (6) as follows: 0.25 formal potassium nitrate solution was added to the charcoal and the mixture was boiled for 2-3 minutes. The solution was decanted into a titration cell and the charcoal was rinsed with potassium nitrate solution; the rinsings were added to the cell. The solution was titrated potentiometrically with silver nitrate. The results of determinations of H are not given.

The charcoal used in these experiments was nutshell (B.S.S. 14-25 mesh) silver impregnated; non-silvered charcoal was not available to them. The charcoal was purified by boiling it repeatedly with distilled water.

The success of the present method depends on the freedom of the charcoal from interfering constituents that will be extracted during the hydrolysis of H. The charcoal used in these experiments (CWS, CII -A, fine) contained 1) chloride, 2) a constituent or constituents which caused an E.M.F. corresponding to less H, and 3) possibly a constituent other than chloride which caused an E.M.F. corresponding to more H. It is seen from Table X that interferences in the determinations of

Table X

Extraction of Interfering Constituents from Charcoal[a]

Charcoal extracted with a solution of KCl in:	Conc. of chloride initially (molal)[b]	Conc. of chloride after extraction (molal)
0.25 formal HNO_3	$2.0 \cdot 10^{-4}$	$3.3 \cdot 10^{-4}$
0.036 " NaOH	1.7 . "	$1.7 \cdot 10^{-4}$
" " "	2.0 "	$2.0 \cdot 10^{-4}$

[a]The procedure is described in a below.

[b]2.0×10^{-4} molal chloride corresponds to 15.9 micrograms of H per ml.

large amounts of H is less when the hydrolysis is made in an alkaline solution than when it is made in an acid solution; hence, in the procedure below (see b) a solution of sodium hydroxide is used.

Because the only available charcoals contained interfering constituents only three experiments were made in which H collected on charcoal was determined. The results are shown in Table XI. In these experiments an air stream containing H vapor was passed through a glass tube containing charcoal and the charcoal was analyzed for H by the procedure

Table XI

Determination of H Collected on Charcoal

Amount of H collected[a] (micrograms)	Amount of H found	Time between collection of sample and determination
1226	1510	1 day
"	1430	1 day
"	1310	5 minutes

[a]Calculated from the concentration of H in the air stream and the time of sampling.

described in b below. The determinations were all high. Two of the samples that were allowed to stand one day before being analyzed were found to contain 23 and 17% more H than was calculated to be present. The sample that was analyzed immediately was only 7% high. These results may indicate that the H on the charcoal hydrolyzed slowly to form HCl which allowed impurities to be extracted from the charcoal during hydrolysis.

Although the data do not look too promising, this method of analysis may be suitable for H adsorbed on charcoal which is relatively free from impurities.

Experimental

a. Extraction of Interfering Constituents from Charcoal. 0.2 g of charcoal were added to sodium hydroxide or nitric acid solution containing a known amount of chloride. The mixture was heated in a bath of boiling water for 10 minutes. The mixture was then centrifuged and the potential of the cell was determined.

b. Determination of H. Absorbing tubes were prepared as described on page 22 except that they contained CWS, C 11 -A- fine charcoal instead of silica gel. The average diameter of the charcoal granules was about 1.4 mm. H vapor in an air stream (see page 22) was passed through the tubes. The samples of charcoal were heated with 0.036 formal NaOH for 10 minutes. The mixtures were centrifuged* and the charcoal was washed three times with dilute NaOH. To the centrifugate and washings were added 2.5 ml of 2.5 formal HNO_3. The chloride was then determined in the cell as described on page 2 .

3. Determination of H Collected in Diethyl Phthalate.

Diethyl phthalate has been shown to be a good liquid for collecting H from air (4). Two methods were used for liberating chloride from H in the phthalate. In the first method the H was hydrolyzed, and in the second the H was oxidized to the sulfone and then hydrogen chloride was removed from the sulfone. The second method gave more accurate results.

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*The charcoal granules contained a charcoal dust which appeared in the solution as a suspension. The potential of the cell fluctuated if the solution was not first centrifuged. However, with other charcoals centrifugation may not be necessary. Perhaps the dust can be removed by washing the charcoal before putting it in the adsorption tube.

A solution of H in diethyl phthalate is quite resistant toward hydrolysis. When a solution of H in diethyl phthalate was heated with water to 95°C for ten minutes very little chloride was found in the aqueous phase. Likewise, when a one phase solution of H in diethyl phthalate acetone and water was heated to 95°C. for ten minutes and more water was added, very little chloride was found in the aqueous phase. However, a corresponding experiment in which glacial acetic acid instead of acetone was used, most of the chloride was liberated. In this experiment equal volumes of 1) a diethyl phthalate solution of H and 2) glacial acetic acid were diluted with water until a second phase just appeared. The mixture was heated. More water was added and the two phases were separated. The aqueous phase contained almost all of the chloride. The concentration of chloride in this solution was determined in the cell. It was found that the E.M.F. of the cell was dependent on large changes in the concentration of the solution. In Table XII are shown the results of experiments in which the potential of the cell was determined for various concentrations of acetic acid, the chloride concentration being held constant. The nitric acid concentration was 0.25 formal.

It is seen that the concentration of acetic acid is critical at about 4.4 formal. The potential has, with respect to the acetic acid concentration, a maximum value at 4.4 formal; if the acetic acid concentration is increased or decreased, the potential falls rapidly. The reason for this behavior is not known.

Table XII

The Effect of Acetic Acid on the E.M.F.

Concentration of chloride (formal)	Corresponding concentration of H (γ per ml)	Concentration of acetic acid (formal)	Temperature (°C)	Observed E.M.F. (mv)
2.10^{-4}	15.9	0	23.0	226
"	"	.88	23.5	225.5
"	"	1.75	"	224
"	"	2.62	"	219
"	"	3.50	"	216
"	"	4.40	"	228
"	"	5.25	"	208
"	"	6.12	"	204
1.10^{-3}	79.5	0	23.0	186
"	"	.88	23.5	186.5
"	"	1.75	23.3	182
"	"	2.62	"	178.5
"	"	3.50	23.5	175
"	"	4.40	23.0	187.5
"	"	5.25	23.4	167
"	"	6.12	"	163

A series of determinations of H in diethyl phthalate was made by hydrolyzing the H in a solution of ethyl phthalate, acetic acid, and water. Then water and nitric acid were added and the concentration of chloride in the aqueous phase was determined. The results are shown in Table XIII. The determinations in which the solution was finally diluted to 0.2 formal acetic acid were more accurate than those in which the final concentration was 4.4 formal. However, in order to hydrolyze the H in 1 ml of diethyl phthalate effectively, about 1 ml of glacial acetic acid (and 0.8 ml of water) must be used; and in order to dilute

Table XIII

Determination of H in Diethyl Phthalate

Amount of H present (γ)	Amount of diethyl phthalate (ml)	Amount of acetic acid (ml)	Time of heating (min)	Final volume (ml)	Final concentration of acetic acid (formal)	Amount of H found (γ)	Amount of H found (%)
1960	1.0	1.0	15	125	0.2	1850	94
1953	"	"	"	100	"	1870	95
"	"	"	"	"	"	1870	95
"	"	"	10	"	"	1870	95
"	"	"	5	"	"	1750	90
"	"	"	10	"	"	706	36
117	3.0	3.0	"	10	4.4	232	198
586	"	"	"	"	"	860	147
977	"	"	"	"	"	1262	129

this solution to 0.2 formal in acetic acid, the final volume must be about 90 ml. Hence, the chloride from H in 1 ml of diethyl phthalate must be finally contained in 90 ml of aqueous solution. Because of this the determination of small quantities of H is difficult.

A more satisfactory method for liberating the chloride from H in diethyl phthalate is the following: The phthalate is stirred with an aqueous solution of potassium permanganate and nitric acid. The H is oxidized to H sulfone. The solution is made alkaline and heated in order to remove hydrogen and chlorine atoms from the H sulfone. Oxalic acid is then added to destroy the permanganate. Nitric acid is then added, the aqueous phase is diluted to a definite volume and the chloride concentration is determined in the cell. Only two determinations were made by this method; the results are shown in Table XIV. The use of permanganate to oxidize H to the sulfone and then alkali to remove the chloride is discussed in the next section (Section 4).

Table XIV

The Determination of H in Diethyl Phthalate[a]

Amount of H present (γ)	Amount of H found, uncorrected (γ)	Amount of H found, corrected[b] (γ)	($\%$)
0	20	0	--
39	70	50	128
78	103	83	106
156	178	158	101
391	378	358	92
1172	1177	1157	99
1953	2075	2055	105

[a]The procedure is described in c below.

[b]Since a potential corresponding to 20 micrograms of H was obtained when no H was present, a correction was applied to all the determinations by subtracting 20 micrograms of H from the amount found. The sodium hydroxide or the oxalic acid may have contained chloride impurities corresponding to this amount of H.

Experimental

a. The Effect of Acetic Acid on the E.M.F. The volumes of a solution of potassium chloride in water, glacial acetic acid, and 2.5 formal nitric acid required to give the concentrations specified in Table XII were stirred together and analyzed by the procedure on page 2 .

b. The Determination of H in Diethyl Phthalate by Hydrolyzing the H. To a solution of H in diethyl phthalate was added an equal volume of glacial acetic acid. Water was then added until a second phase separated.

The ratio of diethyl phthalate to acetic acid to water was about 1 to 1 to 0.8. This mixture was heated in a bath of boiling water for 10 to 15 minutes. The mixture was a single phase while hot. Water and nitric acid were then added to give the volume specified in Table XIII and a nitric acid concentration of 0.25 formal. Ten ml of the aqueous phase were analyzed in the cell by the procedure on page 2 .

c. The Determination of H in Diethyl Phthalate by Oxidizing the H to H Sulfone and Hydrolyzing the Sulfone. Three ml of a solution of H in diethyl phthalate was stirred for five minutes with 2 ml of a solution 0.10 formal in potassium permanganate and 0.2 formal in nitric acid. Five drops of 6 formal NaOH were added and the solution was heated (95°C) for 15 minutes with occasional stirring. One ml of 2.5 formal nitric acid was added and then enough 0.5 formal oxalic acid to decolorize the permanganate. The aqueous phase was diluted to 10 ml and the chloride concentration in the aqueous phase was determined in the cell.

4. Determination of H Collected in Potassium Permanganate Solution

In this method H vapor is recovered from air by passing the air through a bubbler containing an aqueous, acid solution of potassium permanganate. No reference to the use of permanganate solutions as bubbler liquids was found, but experiments (see a below) showed that the solution is quite effective in collecting the H vapor. It is assumed that the H is quickly oxidized in the bubbler to H sulfone and therefore does not volatilize to an appreciable extent.

The chloride can be liberated from the sulfone by adding alkali to the solution and heating it. Under these conditions hydrochloric acid is removed from the H sulfone yielding divinyl sulfone and chloride(7).

The chloride cannot be determined in the cell in the presence of potassium permanganate. For this reason the permanganate is reduced to manganous ion with sodium oxalate before the solution is made alkaline. Neither manganous nor oxalate ions in small concentrations interfere with the determination of chloride in the cell (see b below). Several samples of H in a solution 0.02 formal in potassium permanganate and 0.1 formal in nitric acid were analyzed by the procedure in c below for the purpose of testing this procedure and finding the time of heating necessary to remove the chloride from the sulfone. The results are shown in Table XV.

Table XV

The Determination of H in 0.02 F $KMnO_4$-0.1 F HNO_3

Length of time alkaline solution was heated (Minutes)	Amount of H present (γ)	Amount of H found (γ)	(%)
0	1082	375	34.6
1	"	647	59.7
3	"	998	92.1
5	"	1089	101
10	"	1089	101

Experimental

a. The Recovery of H Vapor from Air by 0.02 F $KMnO_4$-0.1 F HNO_3. An air stream containing an approximately known concentration of H was passed through a bubbler containing 5 ml of a solution 0.02 formal in $KMnO_4$ and 0.1 formal in HNO_3. The apparatus used to provide an air stream containing H has been described in another report (4). The effluent air from the first bubbler was collected in a similar bubbler containing 0.02 F $KMnO_4$-0.1 F HNO_3, or 50% acetic acid, or diethyl phthalate. The recovery by the bubbler was calculated from the equation,

$$\text{recovery} = \frac{\text{H found in 1}}{\text{H found in 1 + H found in 2}},$$

where 1 designates to the first bubbler and 2 designates the second bubbler.

The type of bubbler used is shown in Figure 5 and has been discussed in an OSRD report (4).

Bubbler 1 in every experiment except one contained 5 ml of 0.02 F $KMnO_4$-0.1 F HNO_3; in the other experiment bubbler 1 contained 5 ml of a solution 0.02 F in $KMnO_4$ and 0.1 F in NaOH. Bubbler 2 in five of the experiments contained 0.02 F $KMnO_4$-0.1 F HNO_3; in two of the experiments bubbler 2 contained 50% acetic acid; and in one experiment it contained diethyl phthalate.

The 0.02 F $KMnO_4$-0.1 F HNO_3 solutions were analyzed for H by the procedure in c below. All of the solution in the bubbler was poured into a graduated glass tube and the bubbler was washed with two 1 ml portions of water. The washings were added to the solution.

Table XVI

Recovery of H by Bubblers Containing 5 ml of 0.02 F $KMnO_4$-0.1 F HNO_3

(Temperature 20° C. and flow rate 1 liter per minute unless otherwise stated)

Approximate amount of H delivered[a] (γ)	Relative humidity of air (%)	Concentration of H (γ per liter)	H found in bubbler 1 (γ)	H found in bubbler 2 (γ)	Recovery[b] (%)
1500	0	50	1450	40	97.0
3000	0	"	2700	40	98.5
153	50	15.3	160	0[d]	100.0
3000	50	50	2755	6[d]	99.8
2670[c]	10	"	2230	0[e]	100.0
1500	100	50 then 0 for 2.5 hrs.	1193	202	86
1500	0	50	1217[f]	326	79

[a]Calculated from flow rate and concentration of H in the air.

[b]Calculated from the equation on page 37 .

[c]The bubbler in this experiment was immersed in a water bath at 40°C and the flow rate was 0.5 liter per minute. At the end of the experiment (after 53 liters of air had passed through the bubblers it was found that 2.8 g of water had been lost from bubbler 1 by volatilization.

[d]Bubbler liquid was 50% acetic acid.

[e]Bubbler liquid was diethyl phthalate.

[f]Bubbler liquid was an aqueous solution 0.02 formal in $KMnO_4$ and 0.1 formal in NaOH.

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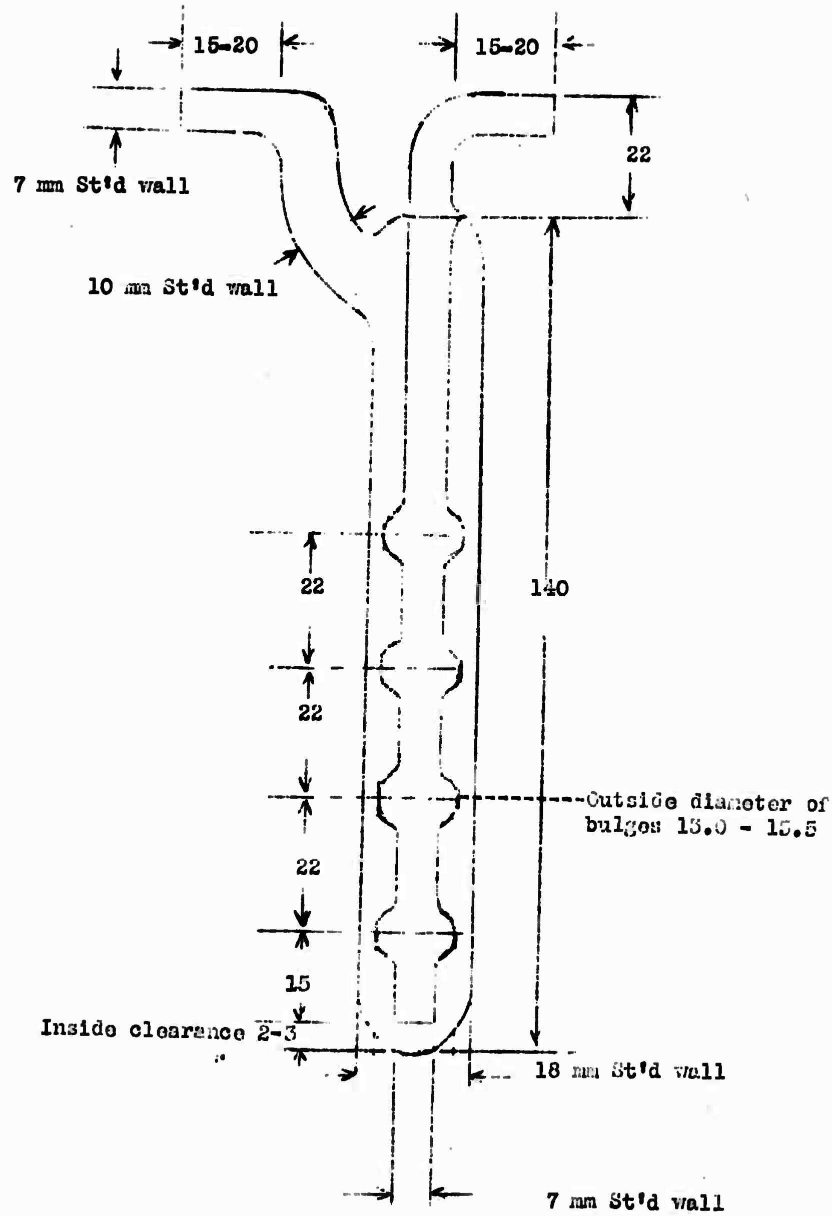
Figure 5. Bubbler



All dimensions are in millimeters

The 50% acetic acid solutions were analyzed by potentiometric titrations with chloramine T (8). The diethyl phthalate solution was analyzed by the DB3 colorimetric method (5). The results are shown in Table XVI.

b. The Effect of Manganous and Oxalic Ions on the E.M.F. The determinations were made by the procedure described on page 2 except that the solution contained the appropriate amount of manganous nitrate and oxalic acid. The results are shown in Table XVII.

c. Procedure for the Determination of H in Potassium Permanganate. Five ml of a solution of H in 0.02 F $KMnO_4$-0.1 F HNO_3 were pipetted into a graduated glass tube. The tube was immersed in a bath of boiling water. One-half formal oxalic acid was added to the solution until it it was colorless, then 3 drops of 6 formal NaOH were added and the solution was allowed to remain in the bath for 5 to 10 minutes. The solution was then made acid with 1 ml of 2.5 formal HNO_3 and was diluted (in the tube) with distilled water. The chloride concentration was then determined in the cell as described on page 2 .

Table XVII

Effect of Manganous and Oxalic Ions on the E. M. F.

Concentration of KCl (formal)	Corresponding concentration of H (γ per ml)	Concentration of $Mn(NO_3)_2$ (formal)	Concentration of oxalic acid (formal)	Observed E.M.F. (mv)
5×10^{-5}	3.98	0	0	254
"	"	.001	"	253
"	"	.005	"	254
"	"	.010	"	254
"	"	.050	"	255
"	"	.005	.0005	254
1×10^{-4}	7.95	0	0	239
"	"	.001	"	238
"	"	.005	"	240
"	"	.010	"	239
"	"	.050	"	241
"	"	.005	.0005	240
2×10^{-4}	15.9	0	0	223
"	"	.001	"	222
"	"	.005	"	223
"	"	.010	"	223
"	"	.050	"	225
"	"	.005	.0005	223
5×10^{-4}	39.8	0	0	143
"	"	.001	"	142
"	"	.005	"	143
"	"	.010	"	143
"	"	.050	"	145
"	"	.005	.0005	143

Part III

DETERMINATION OF HN_3

Discussion

Diethyl phthalate was found to be an effective bubbler liquid for collecting HN_3 vapor from air. Several experiments were made sampling air at 40°C. and 90% humidity; the recoveries of HN_3 were 97-100% (see Table XVIII. An aqueous solution of 0.25 formal nitric acid seems to be an effective absorbent for HN_3, but the solution foams in the bubbler and some solution is lost. Foaming may be due to the lowering of the surface tension by the salt of HN_3. The aqueous solution also has the disadvantage that water is lost from the bubbler by volatilization (see note <u>c</u> to Table XVI, page 38).

The diethyl phthalate solution was analyzed for HN_3 as follows: The HN_3 was extracted with 1 formal nitric acid. An aliquot of the aqueous phase was made alkaline with sodium hydroxide and heated in order to hydrolyze the HN_3. Nitric acid was then added to the solution and the chloride concentration was determined in the cell. The analyses of 3 ml samples of diethyl phthalate solutions containing more than 150 micrograms of HN_3 were accurate to within about 6%. (See Table XIX) The analyses of smaller amounts of HN_3 were less accurate, possibly because of chloride impurity in the sodium hydroxide or in the nitric acid.

An attempt was made to obtain chloride directly from HN_3 in diethyl phthalate by shaking the phthalate with hot aqueous sodium hydroxide solution; the chloride was liberated only slowly and the method was not used for the analysis.

In the analysis of 0.25 formal nitric acid solution for HN3 the solution was made alkaline with sodium hydroxide and then was heated to hydrolyze the HN3. Nitric acid was added and the concentration of chloride was determined in the cell.

Experimental

a. The Recovery of HN3 by Bubblers Containing Diethyl Phthalate or 0.25 Formal Nitric Acid. These experiments were similar to experiments made to determine the recovery of H by bubblers containing potassium permanganate described on pages 37 and 38. An air stream containing HN3 was passed through a bubbler (see Figure 5) containing 6 ml of diethyl phthalate or 6 ml of 0.25 formal nitric acid. The effluent air from the first bubbler was collected in a second bubbler containing the same solvent. The solutions in the two bubblers were analyzed for HN3. If the bubblers contained diethyl phthalate, the solutions were analyzed by the DB3 colorimetric method (5); the DB3 method was used rather than the procedure described in b below because the DB3 method is more accurate. If they contained 0.25 formal nitric acid, the procedure described in c below was used.

The recovery by the first bubbler was calculated from the equation,

$$\text{recovery} = \frac{\text{HN3 found in bubbler 1}}{\text{HN3 found in bubbler 1} + \text{HN3 found in bubbler 2}}.$$

The results are shown in Table XVIII.

Table XVIII[a]

Recovery of HN3 by Bubblers Containing Diethyl Phthalate or 0.25 Formal Nitric Acid

(Temperature 40°C. Relative humidity 90%. Six ml of bubbler liquid were used in each experiment)

Solvent	Approximate amount of HN3 delivered[b] (γ)	Flow rate (liters per minute)	Concentration of HN3 (γ per ml)	HN3 found in bubbler 1 (γ)	HN3 found in bubbler 2 (γ)	Recovery[c] (%)
diethyl phthalate	1100	1	5.5	1120	18	98.4
				1097	13	98.8
"	550	.5	5.5	545	10	98.2
				550	11	98.0
"	110	1	.55	114.5	3.7	96.8
				115	2.7	97.7
				114	1.6	98.6
"	0[d]	1	0	2070	15.1	--
				2040	16.6	--
nitric[e] acid	1100	1	5.5	959	27	97.2
"[e]	550	.5	5.5	550	23	95.8

[a]The experimental work was done by Carl T. Redeman of this laboratory.

[b]Calculated from flow rate and concentration of HN3 in the air.

[c]Calculated from the equation on page 43 .

[d]This experiment was made to test the volatility of HN3 from diethyl phthalate solutions. Bubbler 1 initially contained 2020 micrograms of HN3. Air containing No HN3 was passed through the system.

[e]Some solution was lost due to foaming.

b. Procedure for the Determination of HN_3 in Diethyl Phthalate. Three ml of diethyl phthalate and 5 ml of 1 formal nitric acid were shaken together in a glass stoppered centrifuge tube for 5 minutes. The mixture was centrifuged. A 4 ml aliquot of the aqueous phase was pipetted into a graduated tube, 0.7 ml of 6 formal sodium hydroxide were added to make the solution alkaline, and the tube was immersed in a bath of boiling water for 5 minutes. One ml of 2.5 formal nitric acid was added, the solution was diluted to 10 ml in the tube, and the chloride concentration was determined in the cell. The amount of HN_3 was calculated from the fact that 10^{-5} molal chloride is equivalent to 0.682 micrograms of HN_3 per ml. The results are shown in Table XIX.

Table XIX

Determination of HN3 in Diethyl Phthalate

Amount of HN3 present (γ)	Amount of HN3 found, uncorrected (γ)	Amount of HN3 found, corrected[a] (γ)	(%)
0	20	0	--
27	57	37	137
49	85	65	133
54	89	69	128
99	138	118	119
157	187	167	106
391	400	380	97
782	790	770	99
1173	1150	1130	96
3910	4160	4140	106

[a] A potential corresponding to 20 micrograms of HN3 was obtained when no HN3 was present. This error may be caused by chloride impurity in the sodium hydroxide. A correction was applied to all the determinations by subtracting 20 micrograms from the amount found.

d. The Determination of HN3 in 0.25 Formal Nitric Acid. The contents of the bubbler* were poured into a graduated tube and the bubbler was washed with two portions of water. 0.3 ml of 6 formal sodium hydroxide was added. The solution was heated in a bath of boiling water

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*Before sampling was begun the bubbler contained 6 ml of 0.25 formal nitric acid, but during sampling some water was lost by volatilization. It is assumed that no nitric acid was lost by volatilization.

for five minutes, then 1 ml of 2.5 formal nitric acid was added, and the solution was diluted to 10 ml. The concentration of chloride was determined in the cell.

Only two experiments were made (see Table XVIII). However, it has been shown that the hydrolysis of HN3 is essentially complete in 0.017 formal sodium hydroxide solution at 98°C. in 3 minutes (9).

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TITLE: The Estimation of Chloride by Measuring the E. W. F. of A Silver, Silver Chloride, Ion Half Cell for the Purpose of Estimating H or Other Toxics

AUTHOR(S): Brockman, J.; Lee, T.

ORIGINATING AGENCY: California Inst. of Technology, Pasadena, Calif.

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ABSTRACT:

A method for 1) determining the chloride concentration in an aqueous solution by measuring the potential of a cell composed of a reference half cell and a silver, silver chloride, chloride ion half cell, and 2) determining the H or HN3 by liberating chloride by hydrolysis or by oxidation and then estimating the chloride is described. The procedures used to liberate chloride from H which has been collected on silica gel or charcoal, or in diethyl phthalate or acidified potassium permanganate solution are outlined in detail. The effectiveness of these absorbents and solutions in removing H vapor from air is studied. Procedures are also given for the determination of HN3 using dithyl phthalate or 0.25 F nitric acid as bubbler liquid.

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